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HALOGEN PASSIVATION STUDIES

W. D. English, S. M. Toy, and W. A. Cannon

Astropower Laboratory, Missile & Space Systems Division,
A Division of Douglas Aircraft Company, Inc.

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NOTICES

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FOREWORD

This is the first quarterly progress report prepared under Contract AF 04(611)-10932.

The principal scientists working on the project are: Dr. W. D. English, Principal Investigator; Mr. S. M. Toy; and Mr. W. A. Cannon. They are assisted by Mr. D. E. Nelson, Research Assistant. This report was prepared by Dr. W. D. English, Mr. S. M. Toy, and Mr. W. A. Cannon and approved by Dr. N. A. Tiner, Head of Materials Research Department.

ABSTRACT

This report on halogen passivation studies covers the period from 1 November 1965 to 31 January 1966. During this time, the various alloy powders and sheet stock have been obtained for experimental purposes. Surface area measurements of most of the powdered metals to be used for the kinetic studies have been completed. The constant volume and gravimetric systems to be used for the kinetic studies have been completed. Electro-chemical investigations of the polarization behavior of pure nickel in bromine trifluoride have been started to characterize the passivation of sheet material.

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1.0 INTRODUCTION

Propellant systems which are to handle fluorine or fluorine-containing oxidizers must be passivated before introducing the bulk oxidizers. It is generally conceded that metals which are rendered passive by fluorine or fluorine-containing oxidizers form a thin surface film which is resistant to further chemical attack, although the reaction may continue slowly over a long period of time. The passivation procedures which are specified for propellant systems are generally arbitrary. They involve lengthy exposures of metal surfaces to fluorine or chlorine trifluoride vapor at gradually increasing partial pressure or concentration. It is assumed that the passivation is not permanent and each time a passivated system is exposed to the atmosphere, or is mechanically shocked or flexed, or undergoes a cleaning process, it must be repassivated.

The broad aspects of propellant system passivation must take into account the reaction of the fluorine or fluorine-containing gases with traces of organic matter in the form of solvent residues or lint particles which may inadvertently be left in the system. This is outside the scope of this investigation, however, and here attention is focused only on the reactions with organic-free metal surfaces. However, the possible reactions of passivation films with water or cleaning solvents is an appropriate area of study. This study will involve the investigation of environmental effects on fluoride films which comes under the scope of the contract.

The major objectives of the contract are to obtain new and detailed information on the nature of passivation films on metal surfaces formed by fluorine and certain interhalogens, and to utilize this information to specify improved passivation procedures. The means of obtaining this information will involve detailed investigations of the rates and mechanisms of film formation, of the composition and structure of passive films, and of the environmental conditions leading to the destruction or alteration of passive films.

The initial experimental efforts are aimed at determining the kinetics of passive film formation, including the rates of film growth on various metals in the presence of fluorine and certain interhalogen vapors. From the experimental standpoint, this task is difficult because the passive films, at least

during the initial phase of growth, are extremely thin. It is impossible to determine, employing conventional analytical techniques, the uptake of gas or increase of weight of a bulk metal specimen. Powder metal specimens, having relatively large surface to volume ratio, will be used instead. By employing an area of metal amounting to several square meters, theoretical weight changes can be determined which can be related to film thickness if assumptions are made concerning composition and density of the film. Certain reservations must be held concerning powder metals, in that, due to the method of preparation, the surfaces may not be representative of bulk metals. This factor will be considered, of course, in future interpretation of results.

Recently Astropower Laboratory has become aware that General Chemical Co., in their recommended practices to users of fluorine, no longer suggests that chlorine trifluoride be used for passivating systems. Elemental fluorine is the material of choice.[1] This change was reportedly due to failure to attain complete passivation using CTF in some instances. Perhaps this was due in some measure to the condition reported by J. F. Ellis of the U. K. Atomic Energy Authority. He claims that metal chlorides have been identified in passive films formed with CTF on copper and nickel. Identification was by x-ray crystallography.[2]

2.0 RESULTS AND DISCUSSION

2.1 Materials

The fluorine gas and interhalogens required for the project are at hand and stored at the Gypsum Canyor Fluorine Test Facility.

The sheet stock metals and alloys with the exception of 304 stainless steel and nickel 211, were available from Contract AF33(657)-9162. A supply of 304 stainless steel has been ordered and received. Nickel 211 has been ordered from Wilbur B. Driver Co. A summary of sources and description of sheet materials is given in Table I.

Sources of forgings, castings and welded sheet are being investigated for use later in the program, but no procurement has yet been made.

All the metal and alloy powders have been obtained except AM 350, AM 355, Inconel X and Nickel 211. Commercial sources for these could not be found. A sample of AM 350 is being manufactured to order by the Hoeganaes Sponge Iron Company. Because of the fairly high cost per sample, only the AM 350 was ordered. Previous observations have shown that AM 350 and AM 355 behave similarly in fluorine. The powdered materials currently on hand are described in Table II.

2.2 Apparatus for Kinetic Studies

2.2.1 Constant Volume Apparatus

The constant volume apparatus will be used for determining the rates of fluoride film formation on metal powder exposed to fluorine gas. The schematic diagram of the apparatus is shown in Figure 1.

The construction of this apparatus is complete and requires only installation of the sensitive pressure gage before being put into use. We are awaiting shipment of this gage from the Seegers Instrument Company, Barrington, Illinois. Shipment has been scheduled for February 12, 1966.

TABLE I

MATERIALS FOR HALOGEN PASSIVATION STUDIES

Material	Code Symbol	Supplier & Identification	Condition & Thickness	Composition
Al alloy 2014	B	(Kaiser Aluminum)	T_6 - 0.040	Cu 5.0-39, Mg 0.8-0.2, Mn 1.20-0.40, Fe 1.0 max, Si 1.20-0.50
Al alloy 2024	C	Alcoa Lot #418-731	T_{351} - 0.040	Cu 4.9-3.8, Mg 1.8-1.2, Mn 0.9-0.3, Si 0.50 max, Fe 0.50 max, Cr 0.10 max, Zn 0.25 max
Al alloy 6061	F	Alcoa Lot #703-771	T_6 - 0.040	Cu 0.4-0.15, Mg 1.2-0.8, Mn 0.15 max, Si 0.8-0.4, Fe 0.7 max, Cr 0.35-0.15, Zn 0.25 max
St. Steel 316	J	Republic Steel Heat #49298	Annealed - 0.025	0.06 C, 17.04 Cr, 13.12 Ni, 2.5 mo, 1.52 Mn, 0.27 Si, 0.26 Cu
St. Steel 304	AZ	Republic	Annealed - 0.020	0.063 C, 1.80 Mn, 0.022 P, 0.007 S, 0.69 Si, 18.23 Cr, 8.89 Ni
St. Steel 347	K	Republic Steel Heat #49088	Annealed - 0.025	0.07 C, 17.43 Cr, 10.9 Ni, 1.86 Mn, 0.64 Si, 2.34 Mo, 0.37 Cu, 0.75 (Cb + Ia)
AM 350	N	Allegheny Ludlum Steel Heat #89324	Annealed - 0.025	0.086 C, 16.51 Cr, 4.34 Ni, 2.72 Mo, 0.82 Mn, 0.30 Si, 0.09 N_2
AM 355	O	Allegheny Lublum Steel	Annealed - 0.025	0.14 C, 15.53 Cr, 4.45 Ni, 2.75 Mo, 0.85 Mn, 0.27 Si, 0.12 N_2
Nickel 200	P	International Nickel Heat N9385A	Annealed - 0.025	99.55 Ni, 0.07 C, 0.26 Mn, 0.05 Fe, 0.03 Si, 0.01 Cu
Monel 400	Q	International Nickel Heat N9846	Annealed - 0.025	65.5 Ni, 31.7 Cu, 0.11 C, 0.92 Mn, 1.54 Fe, 0.16 Si

(Continued)

TABLE I (Continued)

MATERIALS FOR HALOGEN PASSIVATION STUDIES

Material	Code Symbol	Supplier & Identification	Condition & Thickness	Composition
Inconel X	R	International Nickel	Annealed - 0.025	0.07 C, 0.05 Mn, 0.25 Si, 0.90 CblTa, 2.62 Ti, 6.45 Fe, 15.00 Cr, Balence Ni
Copper	V	American Brass	Annealed - 0.037	99.46 Cu, 0.01 Fe
Nickel 211	BA	Wilbur B. Driver	Annealed - 0.003	95.2 Ni, 4.5 Mn, 1 Ca, 0.05 Cu, 0.15 Fe, 0.05 Si (Nominal)

TABLE II

POWDERS FOR HALOGEN PASSIVATION STUDIES

Material	Supplier & Identification	Nominal Mesh Size	Composition
St. Steel 304	Plasmadyne Permalloy 213-F SO #5-4766 Lot #Q15415	-325/450	C 0.08 max, Mn 2 max, Si 1 max, P 0.04 max, S 0.030 max, Cr 18-20, Ni 8-11, (nominal)
St. Steel 316	Plasmadyne Plasmalloy #215-F SO #5-4766 Lot #Q10495	-325/450	C 0.08 max, Mn 2 max, Si 1 max, P 0.04 max, S 0.03 max, Cr 16-R, Ni 10-14, Mo.2-3 (nominal)
St. Steel 347L	Metals Disintegrating Corp. #N-2355	-325	C 0.03 max, Cr 17-19, Ni 9-12, Cb 10XC (Nominal)
Nickel 200 A	Plasmadyne Plasmalloy 112-F SO #5-4657 Lot #M-12308	-325/450	Ni 99.5, C 0.06, Mn 0.75, Fe 0.15, S 0.005, Si 0.05, Cu 0.05 (Nominal)
Monel 400	Plasmadyne Permalloy 206-F	-325/450	Not received
Copper	Metals Disintegrating Corp. MD 301 Lot #3137	Atomized Powder	99.9% Cu
Al 6061	Reynolds Metals LS-701 Atomized Powder	-100/325	Mg 0.8-12, Si 0.4-0.8, Cr 0.15-0.35, Cu 0.15-0.40 (Nominal)
Al 2014	Reynolds Metals LS 86 Atomized Powder	-100/325	Cu 3.9-5.0, Si 0.5-12, Mn 0.4-1.2, Mg 0.2-0.8, (Nominal)
Al 2024	Reynolds Metals LS 829 Atomized Powder	-100/325	Cu 3.8-4.9, Mn 0.3-0.9, Mg 1.2-1.8 (Nominal)
AM 350	Hoeganes Sponge Iron Co. (on order)	-325	Not received

Sensitive Gage
0-1500 torr

Standard Gage
0-30 psia

VAC

F_2

He

Union

Ballast
Volume

Sample
Chamber

Hg Manometer
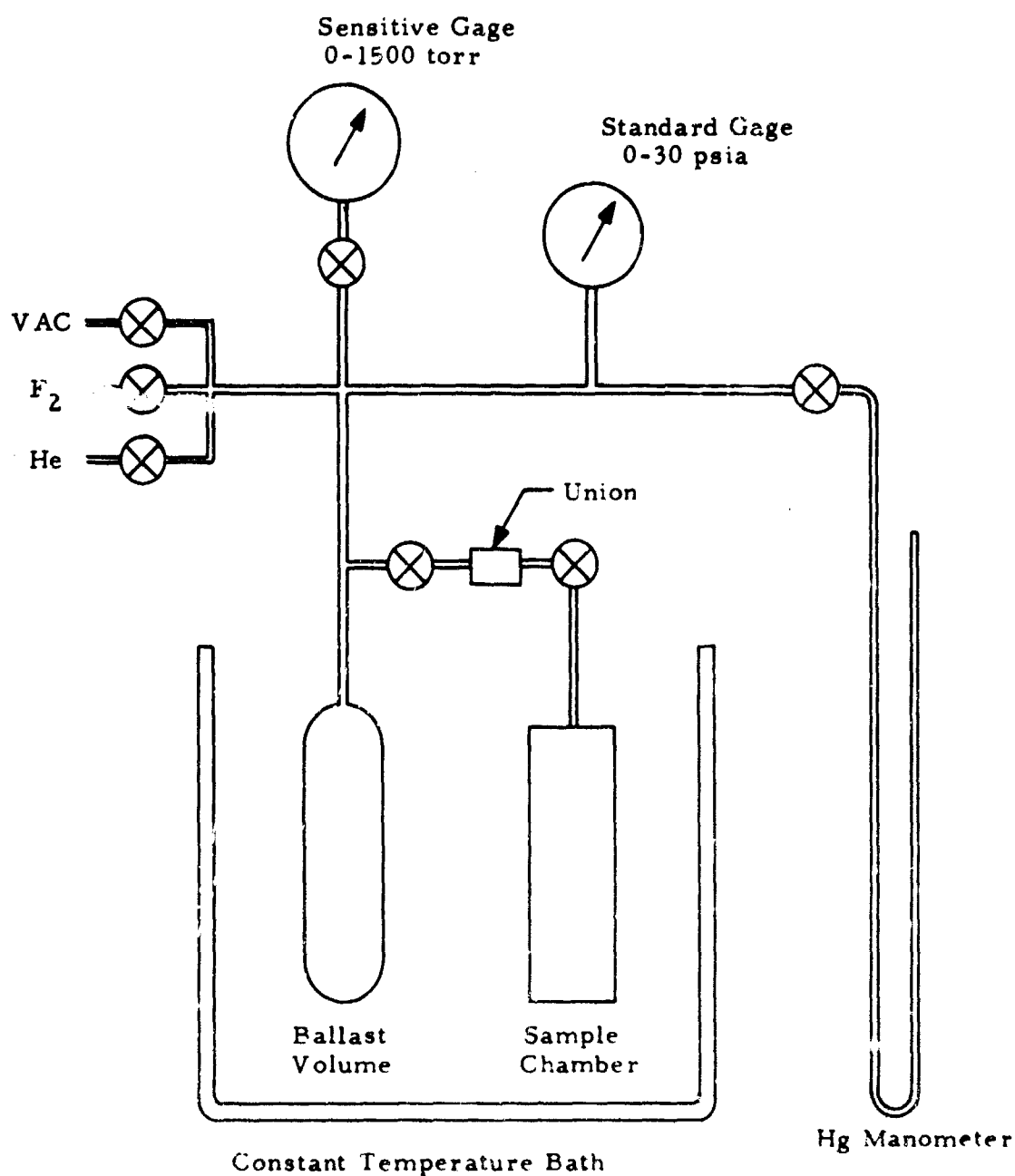
Constant Temperature Bath

Figure 1. Constant Volume Apparatus for Measuring
Reaction Rates of Fluorine with Metal
Powders

The volumes of the ballast chamber and sample chamber are approximately equal — 150 ml each — therefore if the ballast chamber is initially pressurized with gas to about two atmospheres, the final pressure after opening the valves to the evacuated sample chamber will be approximately one atmosphere. The principal of operation is the determination of the change in pressure of fluorine in a constant, known volume as a function of time, as the fluorine reacts with a metal powder contained in the sample chamber. The uptake of fluorine can be related to fluorine film thickness if the total surface area of the reacting metal surface is known.

The procedure is outlined as follows:

1. The apparatus is first passivated without a sample being present.

2. The entire system is purged and evacuated.

3. A metal powder sample is weighed into the sample chamber after which the system is again evacuated.

4. Helium gas is introduced into the system, except the sample chamber, at about two atmospheres pressure. The valves to the sample chamber are opened and the gas expanded into the entire system. If the initial and final pressure is measured accurately with the sensitive pressure gage, this step serves to calibrate the volume of the sample chamber, assuming that the ballast volume and connecting tubing volume are known from prior calibration.

5. The system is again evacuated.

6. Fluorine gas is admitted and step 4 repeated.

7. Pressure in the system is measured as a function of time using the sensitive pressure gage. (This gage is sensitive to ± 1 torr.)

The weight of fluorine, W_F, removed from the gas phase by virtue of reaction with the metal powder, can be computed at any specific reaction time by

$$W_F = MW_{F_2} \cdot N_{F_2} = 38 \frac{\Delta P V_T}{RT}$$

where ΔP is the total change in pressure at the given time and V_T is the total system volume, exclusive of the volume of the powder.

The mean film thickness can be related to W_F as follows:

$$d = \frac{x \cdot W_F}{A\rho} \, 10^8$$

where

d = film thickness in Angstrom units

x = ratio of molecular weights of metal fluoride and fluorine

A = total area of powder specimen in square centimeters

ρ = density of metal fluoride in g/ml.

2.2.2 Flow System for Gravimetric Determination of Reaction Between Halogen Fluoride and Metal Powders

The volumetric method for determining rate of reaction of fluorine with metal powders cannot be used with halogen fluorides because the reaction does not necessarily lead to a net change of pressure in the gas phase. Therefore, we have proposed a gravimetric method for these oxidizers. The flow system shown schematically in Figure 2 has been built.

The halogen fluoride vapor is passed slowly through a glass U-tube which contains a quantity of the metal powder under investigation. The weight change of the tube is determined for various periods of time of exposure from which a plot of mean film thickness as a function of time can be made.

In the system described, four reaction tubes are manifolded in parallel to cover a range of exposure times. Each tube is detachable from the system, and the flow of halogen fluoride through a given tube can be interrupted at any time and the tube purged with nitrogen to arrest further reaction. The detail of the glass reaction tubes is given in Figure 3. The weight gain of the tube is related by the film thickness by the same equation given in Section 2.2.1.

Preliminary experiments were made with fluorine and chlorine trifluoride passed over 304 stainless steel powder (213-F). In these experiments, a small weight loss was obtained rather than the anticipated weight gain. The data for the chlorine trifluoride are given in Table III.
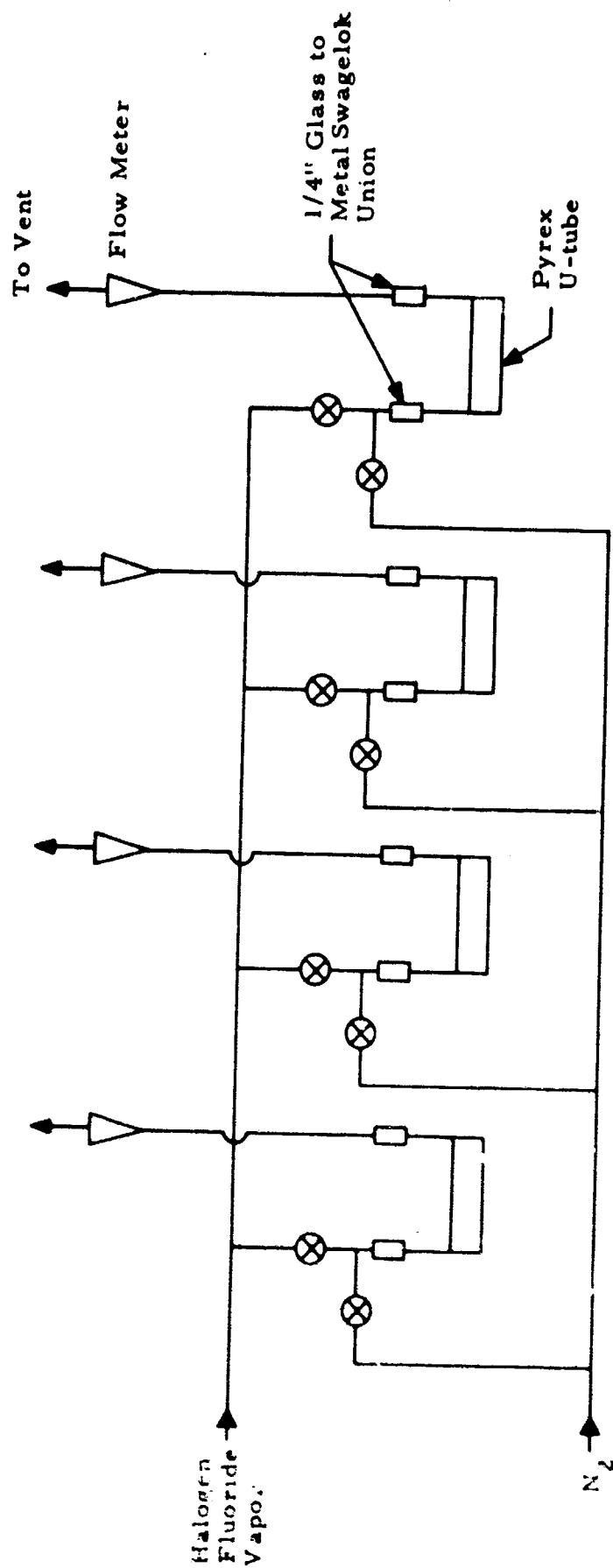
Figure 2. Apparatus for Gravimetric Determination of Rate of Reaction of Halogen Fluorides with Metal Powders

1/4" Medium Wall Pyrex
Tubing
0.250" +0.002"
−0.006"

12 mm
20 mm

60 ± 1 mm

150 mm

20 mm Standard Wall Pyrex
Tubing - Flattened on Bottom
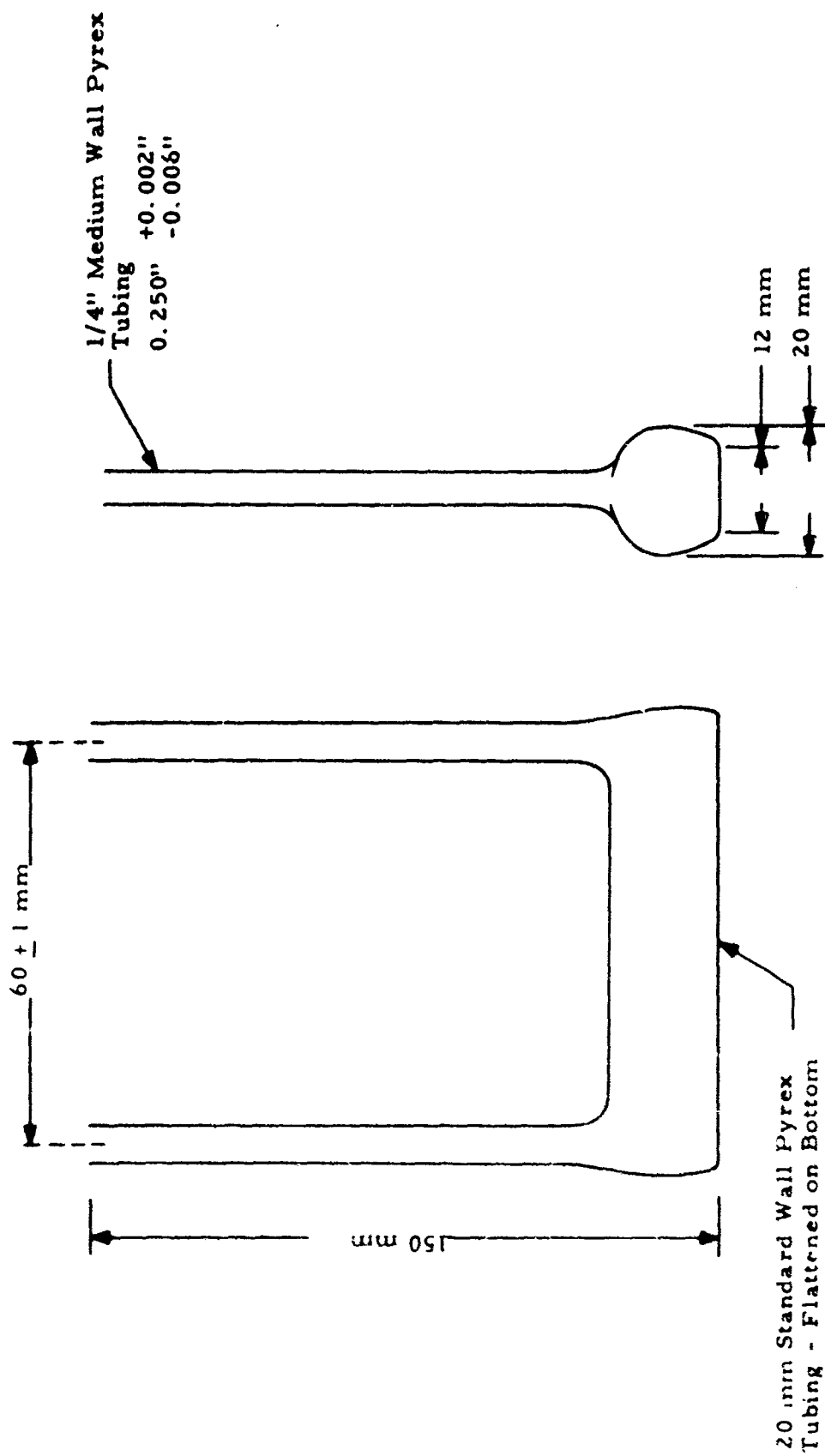
Figure 3. Detail of U-Tubes for Gravimetric Apparatus

TABLE III

FLOW EXPERIMENT

Powder - 40.0g 304-SS (213-F) in each tube
Total Surface area of powder in each tube - 4.04×10^4 cm^2
Vapor - chlorine trifluoride
Flow Rate - Approximately 20 ml/min

Time of Exposure	Initial Weight Tube	Final Weight Tube	Weight Change
15 min	62.9696 g	62.9687 g	-0.0009 g
30 min	63.1964 g	63.1931 g	-0.0033 g
68 min	62.9326 g	62.9216 g	-0.0110 g
150 min	62.3004 g	62.2775 g	-0.0229 g

It was noted that there had been some attack of the glass causing weight losses which more than offset weight gain of the powder. This etching of the glass may come from traces of HF left in the chlorine trifluoride, even though the vapors are passed through a bed of sodium fluoride. It is more likely, however, that the attack is brought about by diffusion of the chlorine trifluoride through the Teflon Swagelok ferrule where the side arms of the U-tube are connected to the stainless steel manifold. The hydrolysis of the chlorine trifluoride outside the ferrule leads to HF attack of the glass side arm. Indeed, visible evidence of etching at this point was noted for those tubes which lost the most weight.

The experimental procedure will be changed to compensate for weight losses of the glass due to HF attack. The metal powder will be weighed into the tube by difference before exposure, and the final weight of powder will be obtained by difference after exposure. Four precise weighings, rather than two, will be required in this method.

2.3 Surface Area Measurements

Knowledge of the specific surface area of the metal powders is basic to the projected kinetic studies where an effort is being made to relate weight gain to thickness of the fluoride film. The B. E. T. method using krypton gas adsorption at $77^{\circ}K$ is a most satisfactory means of determining the specific areas of powder of the type being used in this investigation.

The krypton-gas B. E. T. method makes use of the following adsorption isotherm equation:

$$\frac{P}{V(P_o - P)} = \frac{1}{V_m C} + \frac{(C-1)}{V_m C} \cdot P/P_o$$

where V is the volume of gas adsorbed by a surface at the equilibrium pressure P. P_o is the saturation pressure of the adsorbate, V_m is the volume of adsorbate required to form a monolayer on the surface, and C is a constant for a given adsorbate-adsorbent system.

On typical heterogeneous adsorbents, this two-constant equation can be used with considerable confidence over a limited range of pressures

preceding and following the building up of a monomolecular layer. For any isotherm, or portion of an isotherm, which obeys this relationship, a plot of $P/V(P_o - P)$ against P/P_o will yield a straight line with intercept equal to $1/V_m C$ and slope $(C - 1)/V_m C$. This is the so-called B. E. T. plot. From the slope and intercept, V_m can be calculated; it is equal to the reciprocal of the sum of the slope and intercept.

The total area accessible to adsorption is the product of the total number of gas molecules in V_m and the effective cross-sectional area of each molecule, σ. Therefore:

$$S = \frac{V_m N}{M} \cdot \sigma$$

where S is the total surface area of the absorbent, N is Avogadro's number, and M is the molar volume of the adsorbate. The foregoing equations are the basis of the determination of surface areas by gas adsorption.

The B. E. T. plot also permits the calculation of the constant C in the isotherm equation. From the B E. T. theory, C is given explicitly as

$$C = C_2 \exp (E_1 - E_2)/RT$$

where C_2 is a constant dependent upon the entropy of adsorption, E_1 is the average heat of adsorption of the monolayer, and E_2 is the heat of liquefaction of the adsorbate. The constant C_2 is generally assigned a value of unity.

Because of the simplifying assumptions involved in deriving the B. E. T. equation, the heat of adsorption obtained from the C value is usually considerably lower than the values determined calorimetrically. Heats of adsorption based on the C value can be likened to a sort of average value associated with the less energetic, non-homogeneous part of the surface. Because of the exponential nature of C, its determination from experimental adsorption data is not very accurate. In spite of these limitations, the C value proves quite valuable for comparing different surfaces. A high C value indicates a strong adsorbent-adsorbate interaction, while low C values indicate weak adsorption forces.

Surface area measurements have been completed on most of the powdered metal which will subsequently be used in the kinetic studies. Measurements are made on the powders before and after passivation in fluorine gas. The passivations were carried out by exposing the previously evacuated powder samples to a fluorine pressure of 50 torr for five minutes, then pumping off the residual gas, thereupon admitting increasingly higher pressures of fluorine. The alternate 5-minute exposures and evacuations were repeated at increments of 100, 200, and 400 torr fluorine pressure with a final exposure of one hour at one atmosphere. The exposures were at a temperature of 25°C. Weighed quantities of the metal powders were individually exposed in the tubes shown in Figure 4. This allows passivation, evacuation and subsequent introduction of the powder specimen to the krypton adsorption apparatus without exposure to air. This procedure serves to prevent alteration of the freshly-formed passive film by exposure to moisture in the air.

The results of measurements completed to the date of writing are given in Table IV. Data are also given for samples of 2S aluminum powder and commercial aluminum foil. Although these materials are not included in the list of metals for the subject investigation, the results are presented as pertinent to the study.

The results given in Table IV indicate that within the limits of probable experimental error, there is no change in surface area of the nickel, Monel, 347L stainless steel and copper powders attendant upon passivation with fluorine gas under the conditions described. B. E. T. plots are given in Figures 5 and 6. Inspection of the "C" values reveals that prior to passivation they are quite scattered, and following passivation they tend toward a more constant value. It should be pointed out, however, that "C" values greater than about 100 are grossly inaccurate as calculated from adsorption data. Above about 200 or 300 they assume only rough order-of-magnitude significance. Therefore, with only this limited tabulation available, too much reliance should not be placed on the comparative "C" values for the first four materials. A possible exception to this generalization is the 347L stainless steel which has an unexpectedly low "C" value as received, and which seems to increase significantly upon passivation. It is believed that the difference of

Attachment to Krypton
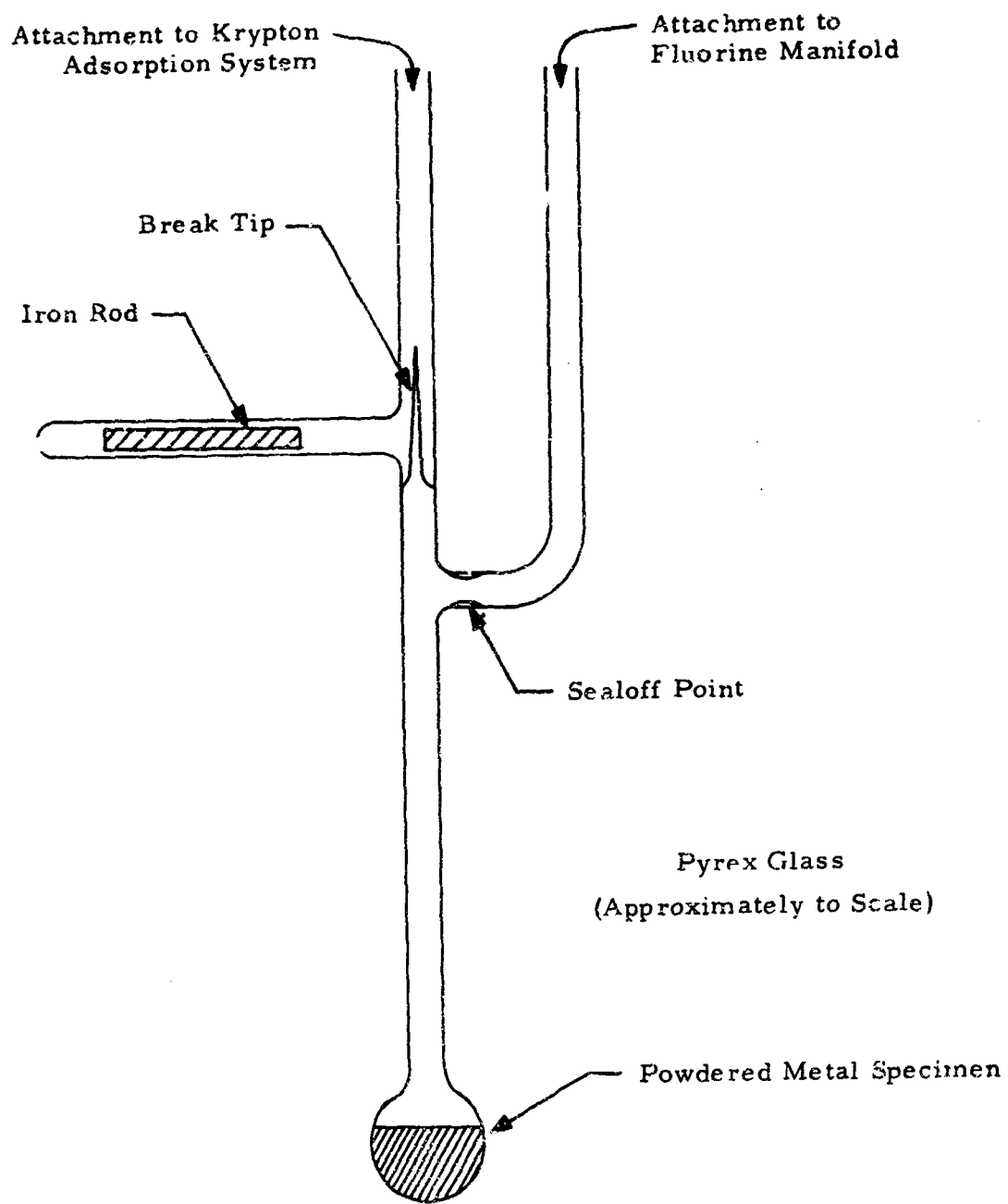Adsorption System

Attachment to
Fluorine Manifold

Break Tip

Iron Rod

Sealoff Point

Pyrex Glass
(Approximately to Scale)

Powdered Metal Specimen

c1421

Figure 4. Apparatus for Determining Surface Area
of Fluorine-Passivated Metal Powder

TABLE IV

SURFACE AREAS OF METAL POWDERS

|	Specific Surface Area cm^2/g	B.E.T. "C" Value	Specific Surface Area cm^2/g	B.E.T. "C" Value
1) Nickel-112F Lot M-12308	2,390	540	2,330	203
2) Monel 206F Lot Q-10435	1,880	155	2,020	143
3) Stainless Steel 347L Lot N-2355	1,570	79	1,490	106
4) Copper DM 301 Lot 3137	2,410	271	2,500	232
5) Aluminum 25 (1)	102	171	700	33
6) Aluminum 25 (2)	1,070	144	710	57
7) Al Foil	1,830*	19	3,260*	73
8) Al 6061 Reynolds	7,800	152	3,460	31
9) 304 Stainless Steel 213F	1,010	92	—	—
10) 316 Stainless 213F	1,040	75	—	—
11) 2014 Al Powder	10,400	251	—	—
12) 2024 Al Powder	4,380	192	—	—

*Total area per specimen
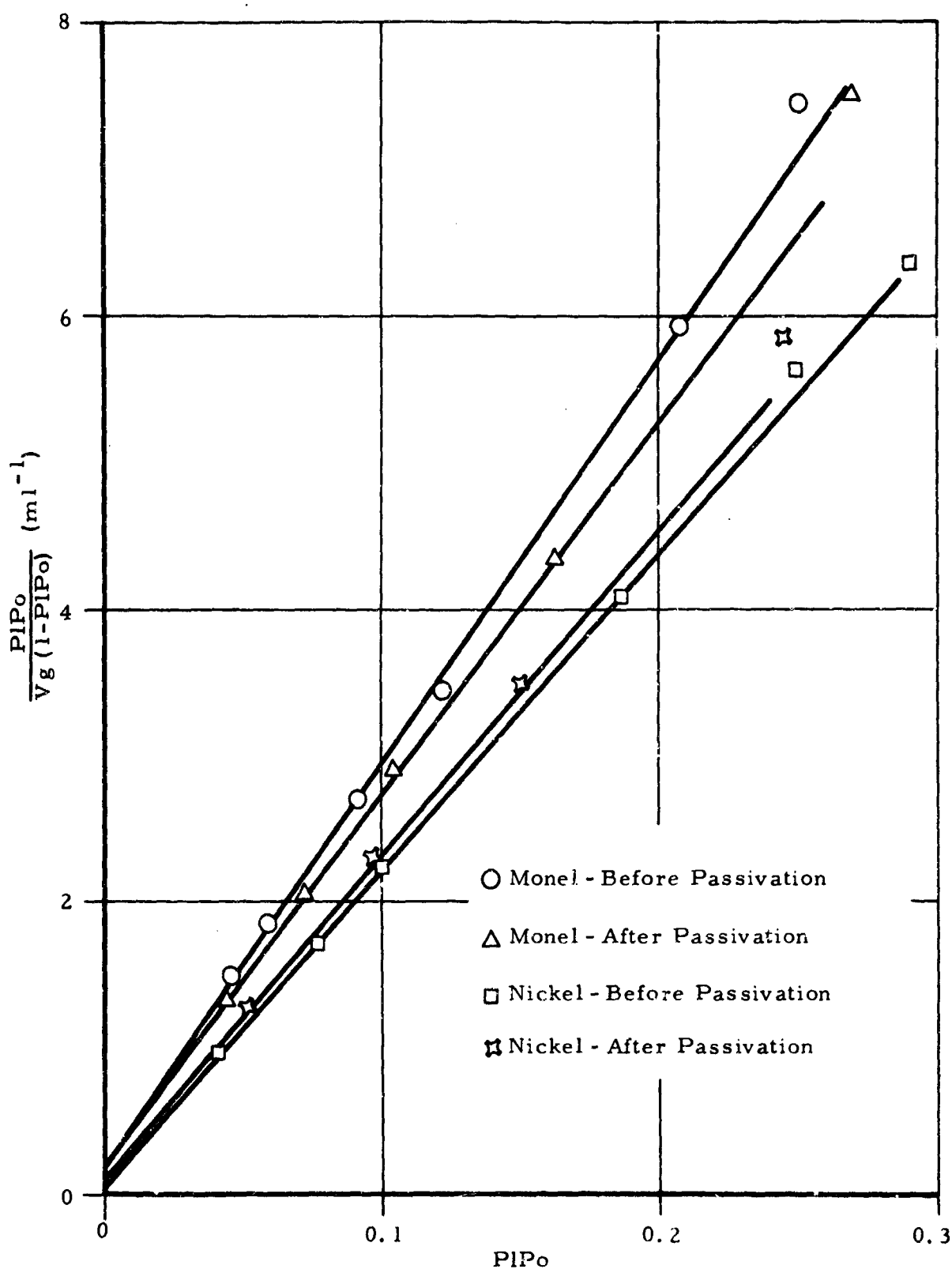
Figure 5. BET Plots. Krypton Adsorption on
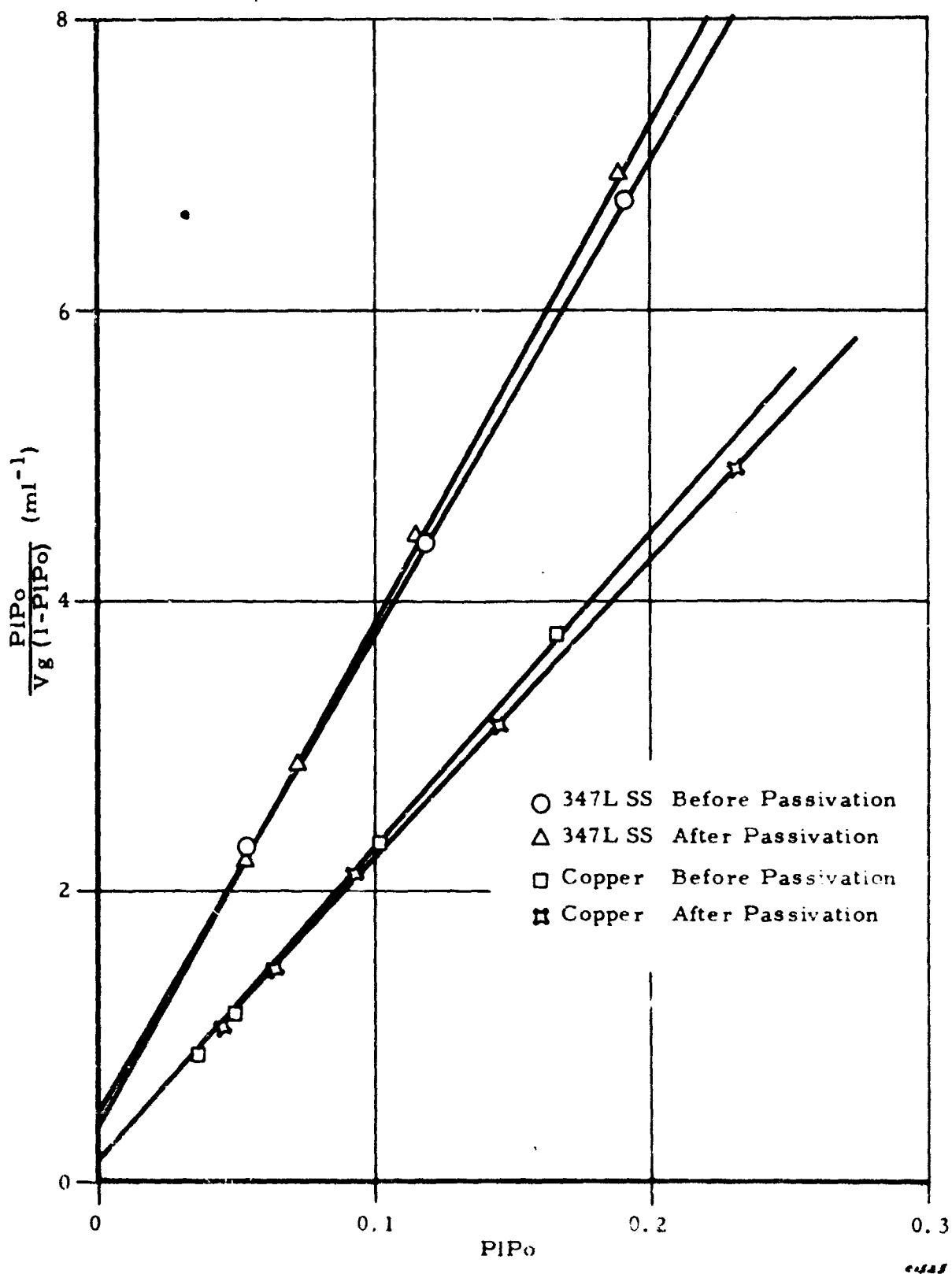Nickel and Monel. $77^{\circ}K$

Figure 6.   BET Plots.   Krypton Adsorption on Copper
and 347L Stainless Steel. $77^{\circ}K$

79 and 106 is greater than the normal limits of experimental error, but additional data will be sought.

For the aluminum samples, large and significant differences are observed in both surface areas and "C" values. B. E. T. plots for the various aluminum materials are shown in Figures 7, 6, and 9. At present these alterations are only partly understood. The 2S aluminum powder sample was run twice because the decrease in surface area was so large upon passivation (ca. 30%) that the results were thought to be subject to a gross error. The results of a second experiment with a new sample and all new apparatus confirmed the first result, however. One or more of several mechanisms may be operative. Some of these are: (1) sintering may occur in the fluoride film during outgassing due to greater mobility of fluoride ions compared to oxide ions in the normal oxide film; (2) a smoothing effect may take place due to greater reactivity of asperities on the surface; (3) the adsorption of krypton on the fluoride film may be anomalous, rendering the use of the B. E. T. equation subject to great error. The fairly low "C" values obtained indicate that the last is a distinct possibility. This can readily be tested by carrying out the adsorption isotherm measurements to higher pressures, and this will be done on later measurements with aluminum alloy materials.

The results obtained with the commercial aluminum foil (Reynolds Wrap) confirm observations made previously in this Laboratory during passivation of aluminum foils and wire with chlorine trifluoride vapor. It is fairly well established that all materials of this type which have been investigated have a chemisorbed fatty acid film on the surface. In addition there is a considerable amount of organic material in excess of the chemisorbed monolayer which seems to be mechanically entrapped in narrow-mouthed pores or microfissures. The latter material is only partly removed by solvent extraction. Even after prolonged solvent extraction, much additional material can be evaporated from the foil under high vacuum at elevated temperature. However, none of the treatments has been successful in removing the chemisorbed film; hence a low "C" value, viz. 19, is obtained which is characteristic of a hydrocarbon surface. Presumably this chemisorbed organic monolayer is chemically removed during treatment with fluorine; hence the final "C" value is much higher.
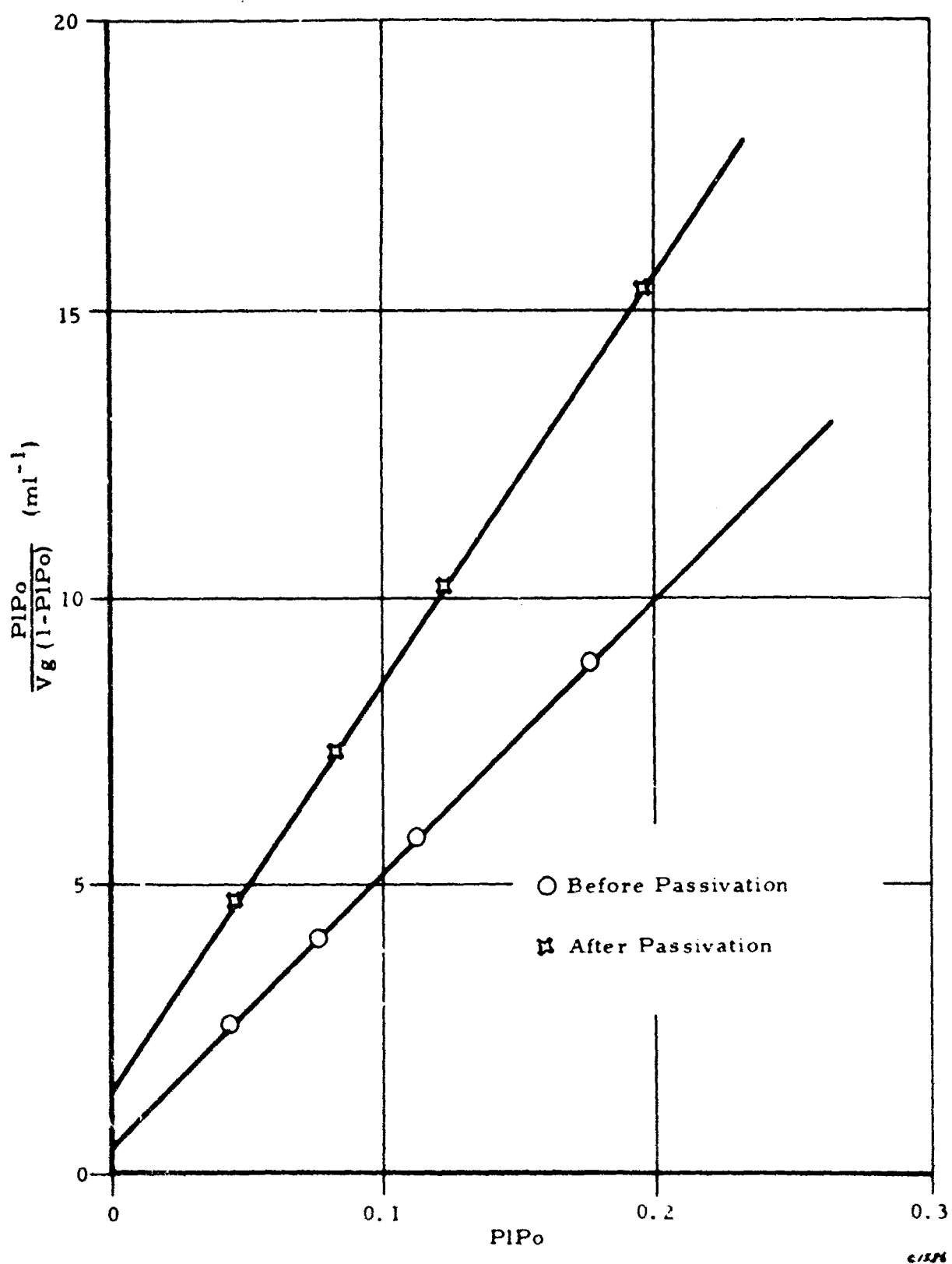
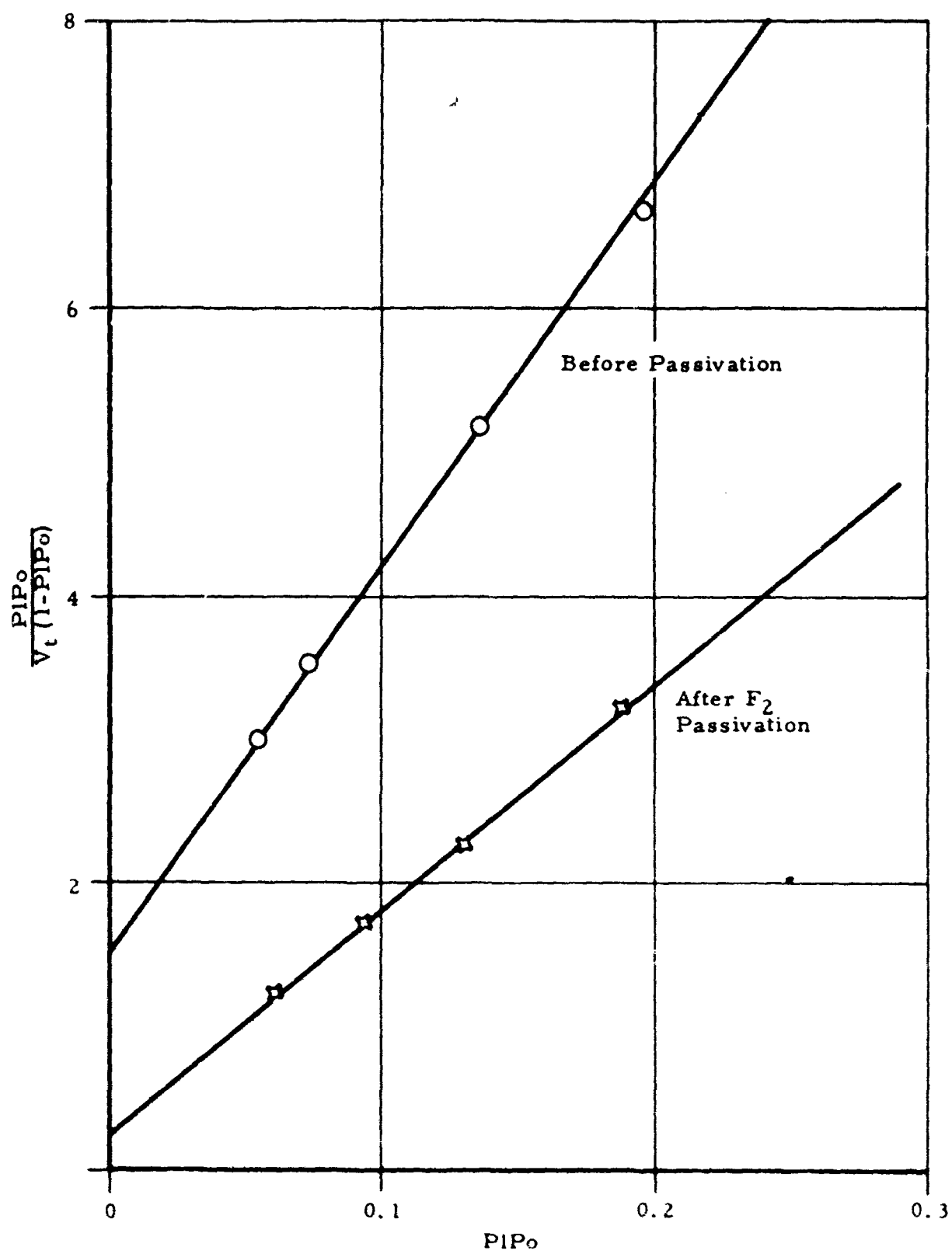Figure 7. BET Plots. 2S Aluminum Powder

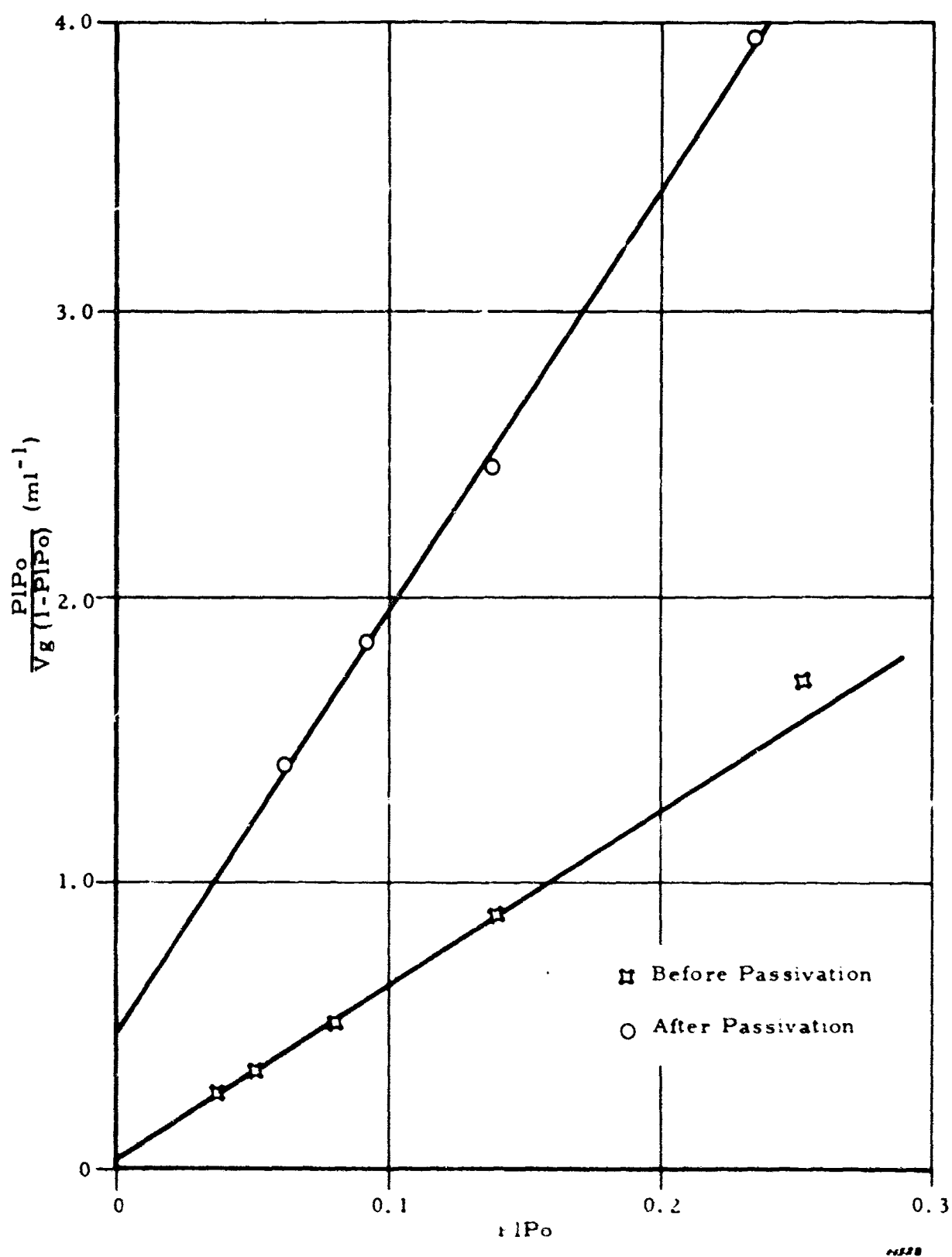Figure 8. BET Plot. Krypton Adsorption on Al Foil. 77°K

Figure 9. BET Plots. Krypton Adsorption on
6061 Al Powder. 77°K

The increase in apparent surface area following the passivation treatment is probably due to one or more of the following factors: (1) removal of organic material from pores and microfissures which opens the walls to adsorption of krypton gas; (2) increase of surface roughness due to etching of the aluminum surface; or (3) etching of the glass sample container from HF produced by reaction of fluorine with organic material.

2.4 Electrode Polarization Measurements

Studies on the anodic polarization of nickel in bromine trifluoride have been previously carried out in this Laboratory. This method of investigation has now been expanded and applied to this contract. The experimental approach involves the study of the anodic polarization behavior of test electrodes in bromine trifluoride. The electrodes under investigation will be subjected to a variety of passivation treatments and environmental effects. The ultimate aim is to define the relationship between the anodic behavior and the nature of the passive films.

Aside from the reactivity of bromine trifluoride, the experimental methods are handicapped by a lack of any suitable reference electrode compatible with this material, and by the fact that it is a passivating medium. Therefore, passivation by exposure to the bromine trifluoride may be superimposed on the passivation produced by exposures to other passivating gases. If these experimental difficulties can be overcome, or compensated for, the electrochemical approach may prove to be a very valuable indication of the quality of passive films.

The polarization cell used in the control experiment with pure nickel electrodes is shown in Figure 10. The working electrode and platinum counter electrode (10 x 10 mm in size) are disposed 5 mm apart. A platinum wire reference electrode is spaced 1 mm away from the working electrode. The cell is constructed of Pyrex glass and requires approximately 20 ml of bromine trifluoride to fill it above the level of the top of the electrodes. The cell is filled by suction from the electrolyte reservoir which communicates with the cell by way of the Teflon plug stopcock. The cell can also be drained when desired by opening the stopcock and allowing the electrolyte to flow back to the reservoir.

6 Volts

200 Ω

MA

V

VTVM

Tubes for filling and
venting cell

Pt Counter
Electrode

Pt Reference Electrode

Working Electrode
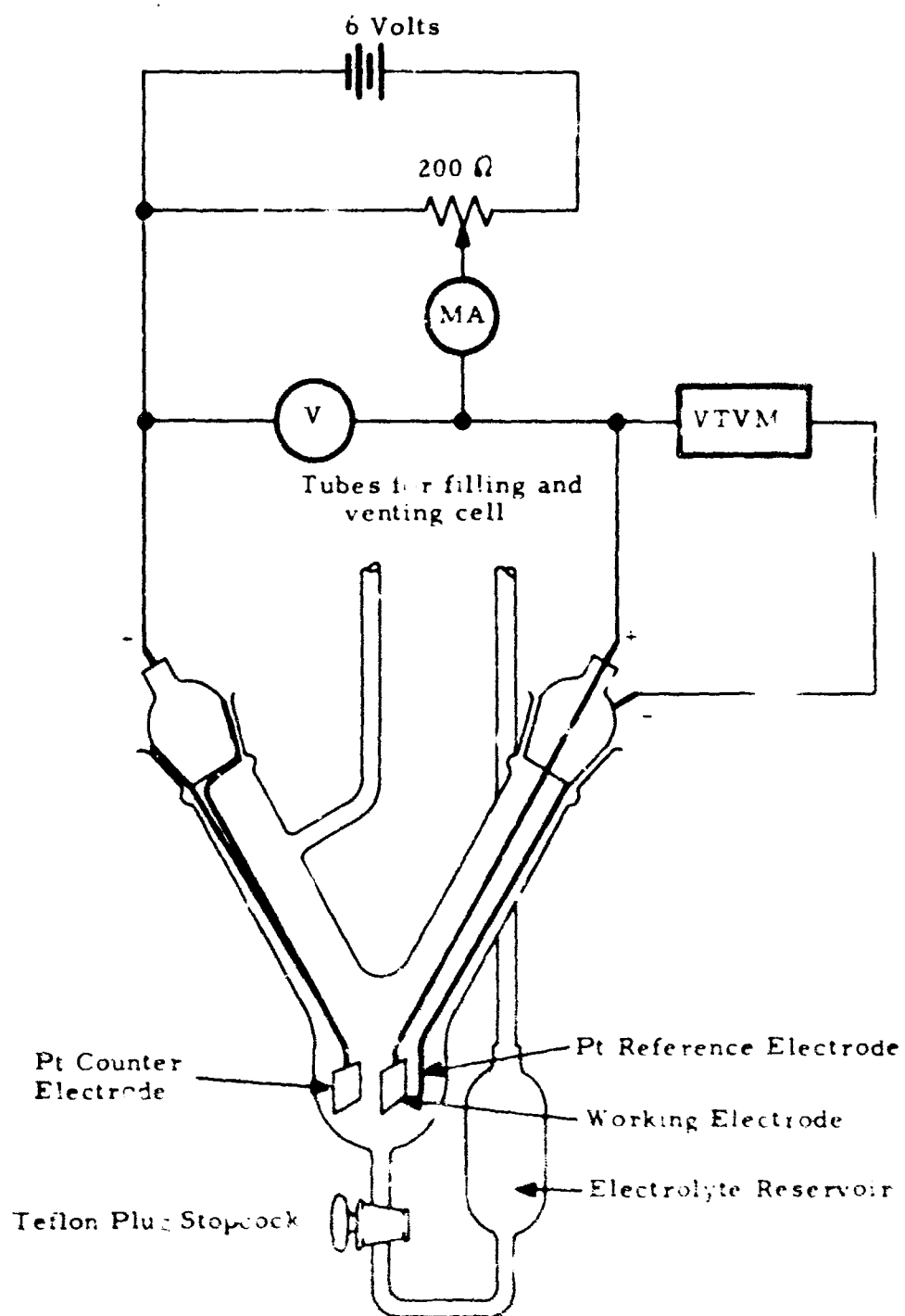
Electrolyte Reservoir

Teflon Plug Stopcock

Figure 10.   Polarization Cell and Circuit

The most noteworthy observation has been the marked difference
between the anodic current for a fresh nickel electrode and one which has been
passivated in fluorine gas for 24 hours. For example, a freshly prepared,
pure nickel working electrode was rinsed in concentrated hydrochloric acid,
then in distilled water, and dried. It was polarized in bromine trifluoride
+3.00 volts with respect to the platinum reference electrode. The anodic
current between the nickel working electrode and the platinum counter electrode
was measured as a function of time of immersion of the electrodes. The anodic
current was observed to fall, rapidly at first and then more slowly, from an
initial value in excess of 3 ma/cm^2 to reach a limiting current density of
about 0.3 ma/cm^2 in approximately one hour. The data are plotted in Figure
11, Curve 1.

The same nickel electrode was rewashed in acid and water, dried
and again returned to the cell, and the polarization repeated. The second set
of data gave Curve II, in general agreement with the first curve except that
final current density was somewhat smaller.

The working electrode was again subjected to the same preparatory
procedure as before, returned to the cell, and exposed to fluorine gas at one
atmosphere at room temperature for 24 hours. Upon repeating the current
density-time experiment, the maximum current density was only slightly over
0.03 ma/cm^2, and it fell rapidly in only six to eight minutes to reach a limiting
current density of about 0.007 ma/cm^2. Therefore, the fluorine-passivated
electrode yielded an anodic current of only a few percent of that of an unpassivated
electrode under the same polarizing voltage. The data are shown in Curve III.

To test the effect of subsequent treatment on a passive surface,
the working electrode was removed from the cell, rinsed copiously with dis-
tilled water, vacuum dried, and returned to the cell. The current density-
time data following this treatment are shown on Curve IV. Although the mag-
nitude of the current density is different from Curves I and II, the shape of
the curves are similar.

The same electrode was then given an HCl rinse, followed by a
water rinse, in the expectation that the electrode would return to a condition
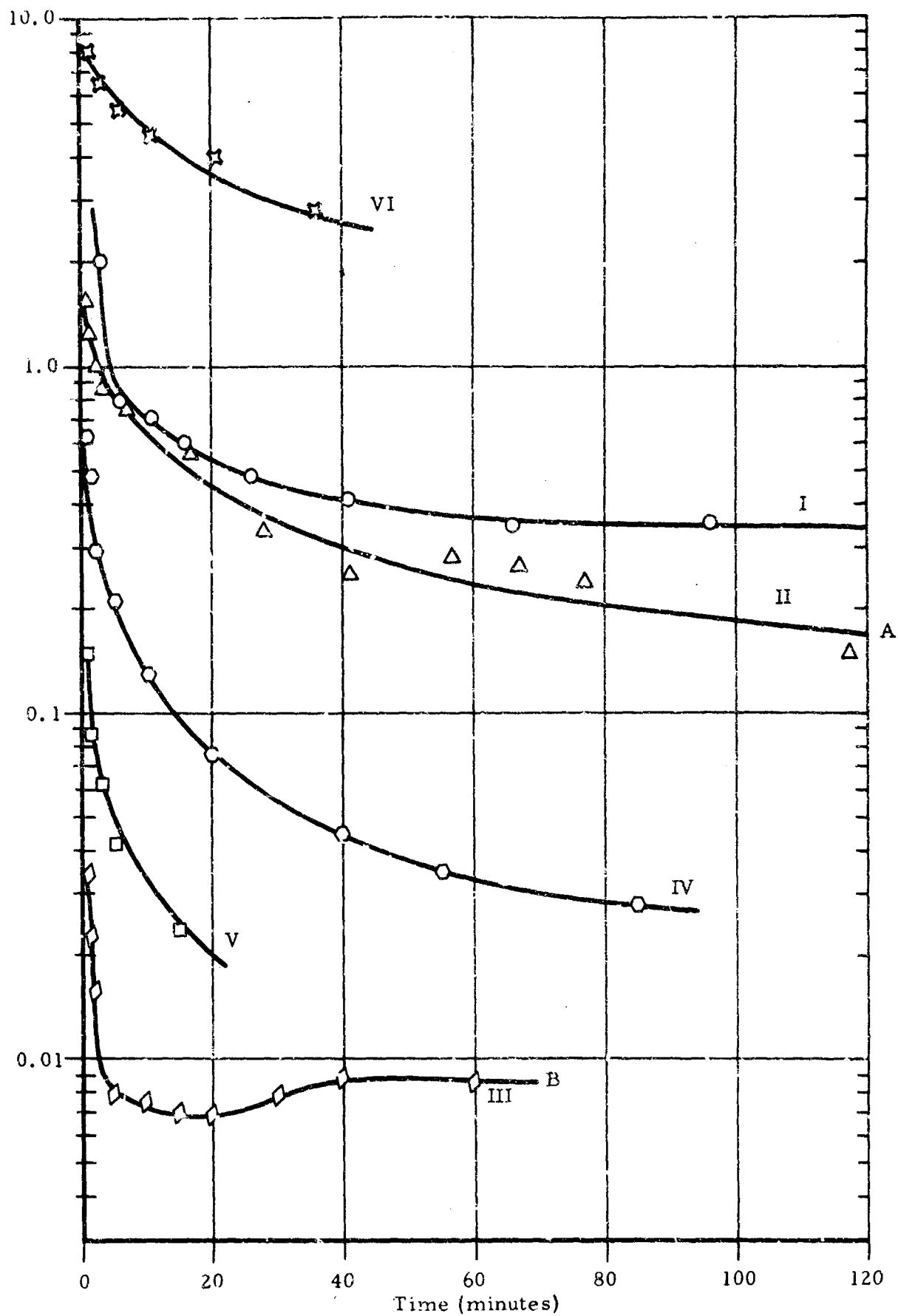near that revealed by Curves I or II. However, the observed current density-

Figure 11. Anodic Current Density Curves for Nickel
Electrodes in BrF_3

time curve is shown at Curve V. Unfortunately due to time limitations, the limiting current density was not reached. No simple interpretation of the behavior of the HCl-washed electrode can be advanced at this time.

Finally, the electrode was removed from the cell, and the surface cleaned and thoroughly abraded with emergy paper, followed by the usual acid and water rinses. The current density or time was then as shown in Curve VI.

It is evident from the data that the initial as well as the approximately limiting current densities vary considerably depending on the surface treatment and history of the electrode. The results with the fluorine treated nickel electrode seem to be unique, however, in that the decrease in current density is much faster.

In addition to the experiment in which the anodic current was measured as a function of time at a constant polarizing voltage, polarization curves were run on the working electrodes at points marked A and B in Figure 11. The polarization curves are given in Figure 12. Curve A was obtained on the unpassivated nickel electrode following the two hours of constant polarization along Curve II of Figure 11, while curve B was obtained following one hour of polarization along curve III of Figure 11.
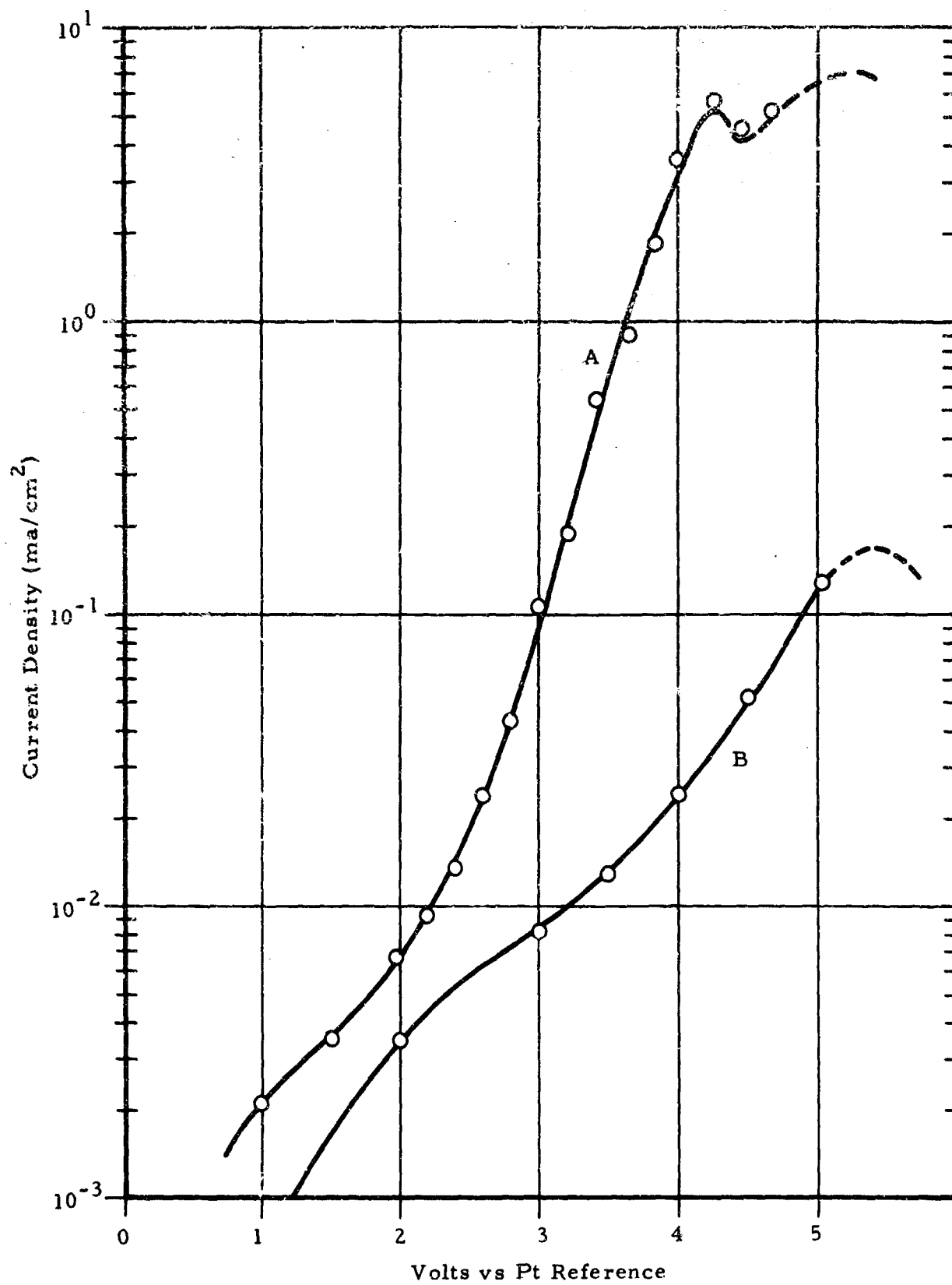
Figure 12. Polarization Curves of Passivated
Nickel Electrodes in BrF_3

3.0 FUTURE WORK

During the next report period, the final checkouts of the constant volume system and gravimetric system for kinetic studies will be completed, and it is expected that much of the projected reaction rate studies between the oxidizer and alloy powder will be completed.

Exposure tests of various alloy coupons will be started, and the characterization of passive films by electron diffraction methods will be initiated.

The electrochemical characterization of passive films will be extended to other electrode materials such as stainless steels, Monel, and aluminum alloys.

REFERENCES

1. Joseph A. Smith, General Chemical Company. Personal communication.

2. J. F. Ellis, United Kingdom Atomic Energy Authority, Technical Section, Preston. Personal communication.

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13. ABSTRACT

This report on halogen passivation studies covers the period from 1 November 1965 to 31 January 1966. During this time, the various alloy powders and sheet stock have been obtained for experimental purposes. Surface area measurements of most of the powdered metals to be used for the kinetic studies have been completed. The constant volume and gravimetric systems to be used for the kinetic studies have been completed. Electrochemical investigations of the polarization behavior of pure nickel in bromine trifluoride have been started to characterize the passivation of sheet material.

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14. KEY WORDS	LINK A		LINK B		LINK C	
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Passivation						
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